

REMARKS

Claim 23 has been amended slightly for consistency. Claims 91, 145, 274 and 292 have been amended consistent with the specification, for example, at page 16, lines 24-25 and page 16, line 32 to page 17, line 9. The dependency of claims 91-94 and 97-99 has been changed. Claims 53-78 and 230-235 have been canceled and new claims 301-354 have been added. Upon entry of this amendment, claims 1-52, 79-229, 236-244 and 247-354 will be pending in the application.

No new matter has been introduced by the present amendments.

Support for new claims 301-304, 311-314, 321-324, 329-332, 339-342 and 349-352 may be found, for example, at page 14, line 25 to page 15, line 22 of the specification.

Support for new claims 305-310, 315-320, 325-328, 333-338 and 343-348, 353 and 354 may be found, for example, at page 16, line 24 to page 18, line 14 of the specification.

Applicants reserve the right to pursue the subject matter of the canceled claims in a continuing application.

Allowed and Allowable Subject Matter

Applicants acknowledge the allowance of claims 13-52, 79-99, 206-229, 236-241 and 256-300. New dependent claims 311-354 are likewise submitted as in condition for allowance.

Applicants further acknowledge the indication of allowable subject matter in dependent claims 5, 66-74, 78 and 106-199. Claims 66-74 and 78 have been canceled.

Rejections Under 35 U.S.C. §103(a)

Reconsideration is respectfully requested of the rejection of claims 1-4, 6-12, 100-105, 200-205, 242-244 and 247-255 under 35 U.S.C. §103(a) as unpatentable over EP 0 019 445 (Nitrokemia) in view of U.S. Patent No. 4,264,776 (Hershman et al.), van Dam et al. (*Journal of Catalysis*, 1991) and U.S. Patent No. 4,624,937 (Chou). As noted above, rejected claims 53-65, 75-77 and 230-235 have been canceled without prejudice.

The rejections under 35 U.S.C. §103(a) of claims 100-143, 242-244 and 247 as unpatentable over Nitrokemia in view of Hershman et al., van Dam et al. and Chou in further view of U.S. Patent No. 6,153,753 (Johnson et al.) and of claims 1-99, 200-241 and 248-300 as unpatentable over Nitrokemia in view of U.S. Patent Nos. 4,186,110 (Jalan et al.) and 5,876,867 (Itoh et al.), Hershman et al. and Chou that were made in the December 2, 2003 Office action are not continued in the present Office action and are presumed withdrawn.

Claims 1, 248 and 252

As noted in Amendment D submitted June 2, 2004, the noble metal on carbon catalyst (optionally including a promoter) utilized in the claimed oxidation processes exhibits what applicants refer to as "deeply reduced" characteristics. Applicants have discovered that, by use of such deeply reduced catalysts satisfying the various requirements set forth in the claims, reagents such as N-(phosphonomethyl)iminodiacetic acid (PMIDA) or salts thereof can be effectively oxidized without undue loss of noble metal from the carbon support in the course of a catalytic oxidation reaction, particularly when conducted in an aqueous medium capable of solubilizing a noble metal. The improved resistance to solubilization of the noble metal provided by using a deeply reduced catalyst in accordance with the present invention overcomes a significant obstacle which has previously compromised the economic feasibility of using a noble metal on carbon support to catalyze oxidation reactions. Use of a deeply reduced noble metal on carbon catalyst in the oxidation of PMIDA or a salt thereof provides for substantially quantitative oxidation to N-(phosphonomethyl)glycine (glyphosate) or its salts and effective oxidation of the C₁ by-products of the reaction (formaldehyde and formic acid) to be maintained for a prolonged period and/or over numerous oxidation cycles without the excessive loss of noble metal as is otherwise typically encountered in acidic aqueous oxidation media.

Independent claims 1, 248 and 252 are directed to processes for the catalytic oxidation of a reagent by contacting the reagent with an oxidation catalyst in the presence of oxygen, wherein the oxidation catalyst comprises a noble metal at the surface of a carbon support. In claim 1, the reagent is N-(phosphonomethyl)iminodiacetic acid or a salt thereof which is oxidized to prepare glyphosate or a salt thereof. In claims 248 and 252, the reagent is oxidized in a mixture that is able to solubilize a noble metal and the catalyst utilized in claim 252 further comprises a promoter at the surface of a carbon support. The deeply reduced noble metal on carbon catalyst used to catalyze the oxidation reaction in each of independent claims 1, 248 and 252 is characterized such that the catalyst yields no more than about 1.2 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst, after being heated at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere and before being exposed to an oxidant following the heating in the hydrogen atmosphere, is heated in a helium atmosphere from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes. To provide a catalyst satisfying this recited maximum carbon monoxide desorption yield, the catalyst may be "deeply reduced" utilizing the high-temperature gas-phase reduction treatment and various other catalyst preparation techniques described in the specification and the working examples of the application.

On page 2 of the December 30, 2004 Office action, the Examiner indicates allowed or allowable subject matter in various claims requiring use of a catalyst having a ratio of carbon atoms to oxygen atoms of at least about 20:1 at the surface of the catalyst including, for example, independent claim 13 or claims requiring use of a catalyst prepared by depositing a noble metal at a surface of a carbon support having a ratio of carbon atoms to oxygen atoms of at least about 20:1 at the surface of the support including, for example, independent claim 49. These claims are indicated as allowed or allowable, at least in part, on the basis of the improved resistance to solubilization of the

noble metal provided by deeply reduced catalysts exhibiting this minimum carbon to oxygen atom surface ratio as shown, for example, by the data presented in Tables 5 and 7 of Examples 7 and 9 of applicants' specification.

Applicants respectfully submit that the process as defined in independent claims 1, 248 and 252 and the claims depending therefrom are patentable over Nitrokemia, Hershman et al., van Dam et al. and Chou for the reasons already of record. Furthermore, applicants submit that it is their discovery that measuring the amount carbon monoxide desorbed from a catalyst subjected to high temperatures is an effective alternative to measuring the carbon to oxygen atom surface ratio as a means of assessing the amount of detrimental oxygen-containing functional groups at the surface and predicting noble metal retention and maintenance of catalyst activity (See, for example, applicants' specification at page 9, line 26 to page 11, line 18). More particularly, the deeply reduced catalyst used in accordance with one embodiment of the present invention yields no more than about 1.2 mmole of carbon monoxide per gram of catalyst, more preferably no more than about 0.7 mmole of carbon monoxide per gram of catalyst, even more preferably no more than about 0.5 mmole of carbon monoxide per gram of catalyst and especially no more than about 0.3 mmole of carbon monoxide per gram of catalyst when a dry sample of the catalyst is heated in a helium atmosphere from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes. As taught by applicants, carbon monoxide desorption yield as a measure the amount of detrimental oxygen-containing functional groups at the surface is readily determined by thermogravimetric analysis with in-line mass spectroscopy (TGA-MS) and preferably, as called for in claims 1, 248 and 252, is determined after the catalyst is reduced by heating at a temperature of about 500°C for about 1 hour in a hydrogen atmosphere.

In response to the invitation by the Examiner in the paragraph bridging pages 3 and 4 of the Office action, applicants direct the Examiner's attention to Example 8 beginning on page 59

of applicants' specification. In this Example, the concentration of oxygen-containing functional groups at the surface of various platinum on carbon catalysts was assessed by measuring carbon monoxide desorption yield through TGA-MS under helium using the claimed heating protocol. The catalysts were then used in a single-cycle PMIDA oxidation reaction and the amount of platinum leached into the reaction solution per gram of glyphosate produced ($\mu\text{g Pt/g glyphosate produced}$) was also measured. The results are tabulated in Table 6.

All the catalyst used in Example 8 were based on a platinum on carbon catalyst (Aldrich Catalyst #33015-9), but were subjected to various reduction treatments prior to analysis. The first catalyst sample listed in Table 6 was subjected to applicants' preferred high-temperature gas-phase reduction treatment (See, for example, page 32, line 10 to page 34, line 4 of applicants' specification) by heating the catalyst at a temperature of 640°C in 20% hydrogen for six hours. The second catalyst sample listed in Table 6 was also subjected to the same preferred high-temperature gas-phase reduction treatment in combination with an ammonia pre-wash. The third catalyst sample was heated only to 75°C in 20% hydrogen for six hours and the fourth catalyst sample was not heated at all, but subjected to an ammonia pre-wash. The fifth catalyst sample reported in Table 6 was analyzed and used as received.

The first and second catalyst samples exhibited carbon monoxide desorption yields below the 1.2 mmole CO/gram catalyst maximum in accordance with claims 1, 248 and 252 (i.e., 0.41 and 0.38 mmole CO/gram catalyst, respectively), and noble metal leaching as measured by platinum in the reaction solution of 5.2 and 5.3 $\mu\text{g Pt/g glyphosate produced}$, respectively. Advantageously, these two catalysts demonstrated strong retention of catalyst activity in oxidizing the formaldehyde byproduct as shown by the measured 13.78 and 15.70 mg of formaldehyde per gram of glyphosate produced, respectively. By contrast, the third, fourth and fifth catalyst samples listed in Table 6 exhibited carbon monoxide desorption yields well above the claimed 1.2

mmole CO/gram catalyst maximum (i.e., 1.87, 1.59 and 1.84 mmole CO/gram catalyst, respectively). Significantly, this increase in carbon monoxide desorption yield was accompanied by an over five-fold increase in noble metal leaching as measured by platinum in the oxidation reaction solution. As a result of noble metal losses, each of the latter three catalyst samples reported in Table 6 showed a demonstrably reduced formaldehyde oxidation activity as shown by the measured 19.85, 22.73 and 19.39 mg of formaldehyde per gram of glyphosate produced, respectively.

The results shown Table 6 clearly demonstrate and confirm applicants' teaching that carbon monoxide desorption yield exhibited by a catalyst is correlated and predictive of noble metal retention and maintenance of catalyst activity, the latter generally increasing as the carbon monoxide desorption yield decreases. More specifically, these results demonstrate that noble metal on carbon catalysts exhibiting a carbon monoxide desorption yield below the 1.2 mmole CO/gram catalyst maximum recited in claims 1, 248 and 252 provide significantly improved resistance to noble metal leaching as compared to catalysts exhibiting a carbon monoxide desorption yield in excess of about 1.2 mmole CO/gram catalyst.

To the extent the Examiner contends that the results presented in Table 6 of Example 8 do not sufficiently closely correlate a maximum carbon monoxide desorption yield of about 1.2 mmole CO/gram catalyst as called for in claims 1, 248 and 252 with decreased noble metal leaching, applicants respectfully submit that the experimental results clearly establish the direct relationship between increased measured carbon monoxide desorption yield and the severity of noble metal leaching. As noted above, carbon monoxide desorption yield is merely an alternative to carbon to oxygen atom surface ratio as a means of assessing the amount of oxides and other detrimental oxygen-containing functional groups at the surface of the catalyst that may lead to increased noble metal losses. As agreed to by the Examiner on page 4 of the Office action, the removal of oxides and other detrimental oxygen-containing functional groups from

the surface of the carbon support as a means for solving the noble metal leaching problem would not have been appreciated by one of ordinary skill in the art based on the disclosure in Chou. Accordingly, a maximum carbon monoxide desorption yield as a measure of the amount detrimental oxygen-containing functional groups that may be tolerated in the practice of the present invention without undue noble metal losses would likewise not have been appreciated by one of ordinary skill in the art. This is particularly the case here since Chou provides no teaching or motivation for utilizing the activated carbon catalyst disclosed therein as a support for a noble metal as called for in the instant claims. Moreover, a person practicing the techniques for preparing a noble metal on carbon catalyst disclosed in the other cited references would not necessarily obtain a catalyst exhibiting a carbon monoxide desorption yield of no more than about 1.2 mmole CO/gram catalyst as called for in independent claims 1, 248 and 252. None of the cited references provide any basis for the discovery that deeply reduced noble metal on carbon catalysts exhibiting the claimed maximum carbon monoxide desorption yield would reduce metal loss and would be commercially effective for the conversion of reagents such as N-(phosphonomethyl)iminodiacetic acid to glyphosate with minimal loss of noble metal.

In view of the above, independent claims 1, 248 and 252 are respectfully submitted as patentable over Nitrochemia in view of Hershman et al., van Dam et al. and Chou. Claims 2-4, 6-12, 249-251, 253-255 and 311-320, which depend directly or indirectly from claim 1, 248 or 252, are likewise submitted as patentable over the cited references.

Claim 100

On page 4 of the Office action, it is asserted that an additional reference is not necessary to teach the limitation of "a continuous reaction." However, claim 100 does not simply require continuous oxidation of N-(phosphonomethyl)iminodiacetic

acid or a salt thereof.¹ More particularly, independent claim 100 is directed to a process for the preparation of N-(phosphonomethyl)glycine or its salts by oxidation of N-(phosphonomethyl)iminodiacetic acid or a salt thereof and requires, *inter alia*, continuously contacting an aqueous feed stream comprising N-(phosphonomethyl)iminodiacetic acid or a salt thereof with an oxygen source in a stirred tank reactor of a continuous reactor system (i.e., a CSTR) and in the presence of a particulate catalyst comprising a particulate carbon support having a noble metal at a surface of the carbon support.

Applicants respectfully submit that the cited references, either alone or in combination, fail to teach all of the features recited in the process defined in claim 100 such that a *prima facie* case of obviousness is lacking. That is, Nitrokemia, Hershman et al., van Dam et al. and Chou fail to teach or suggest continuously contacting an aqueous feed stream comprising N-(phosphonomethyl)iminodiacetic acid or a salt thereof with an oxygen source in a stirred tank reactor of a continuous reactor system and in the presence of a noble metal on carbon catalyst.

Contrary to the assertion in the Office action, Chou does not teach "continuous oxidations with heterogenous catalysis." In each of the examples of Chou, the oxidation of N-(phosphonomethyl)iminodiacetic acid using the carbon only catalyst was carried out in **batch fashion** in an autoclave reactor. That is, rather than continuously contacting an aqueous feed stream containing N-(phosphonomethyl)iminodiacetic acid with an oxygen source as called for in claim 100, the autoclave was charged with all of the N-(phosphonomethyl)iminodiacetic acid, water and carbon and then oxygen was introduced and contacted

¹ Indeed, such a claim would not be novel in view of the disclosure in U.S. Patent No. 3,969,398 (Hershman) of contacting an aqueous solution of N-(phosphonomethyl)iminodiacetic with molecular oxygen and an activated carbon catalyst in a tubular continuous reactor packed with activated carbon (See pages 21-24 of applicants' Amendment C filed March 25, 2002; and col. 2, lines 20-21 and Example 5 of Hershman '398). Similar disclosure appears in Hershman et al. '776 at col. 3, lines 6-8.

with the reaction mixture for a finite period of time until the reaction was complete at the end of the batch.

Moreover, the observation in the Office action that Nitrokemia "teaches the reaction in a continually shaken tank reactor" misconstrues the reference and its relevance to the process defined in claim 100. The disclosure in Nitrokemia that the oxidation is always carried out under shaking or stirring (See, for example, col. 4, lines 19-20 of Nitrokemia) does not teach or suggest a process as defined in claim 100 in which an aqueous feed stream containing N-(phosphonomethyl)iminodiacetic acid is continuously contacted with an oxygen source. Like Chou, the description and examples of Nitrokemia are limited to carrying out the oxidation reaction in **batch fashion** including charging the steel reaction vessel or tank with all of the N-(phosphonomethyl)iminodiacetic acid, water and catalyst and then introducing and contacting oxygen with the reaction mixture with shaking or stirring for a finite period of time until the reaction is complete at the end of the batch. A feed stream of additional N-(phosphonomethyl)iminodiacetic acid is not introduced into the tank so as to be continuously contacted with oxygen as called for in claim 100.

The only reasoning for the continued rejection of claim 100 is the unsupported assertion on page 4 of the Office action that it would be within the scope of the artisan to select any common industrial reactor, such as a CSTR, for such a process with a reasonable expectation of success. However, as noted above, the attempted reliance on the disclosure in Chou or Nitrokemia fails to teach or suggest conducting the oxidation of N-(phosphonomethyl)iminodiacetic acid in anything other than a batch mode and certainly does not teach or suggest conducting the reaction in a CSTR of a continuous reactor system in which an aqueous feed stream containing N-(phosphonomethyl)iminodiacetic acid is continuously contacted with an oxygen source. van Dam et al. likewise does not suggest the process as defined in claim 100.

The teaching in Hershman et al. of contacting the N-(phosphonomethyl)iminodiacetic acid reactant with oxygen and carbon catalyst in a continuous tubular reactor packed with the catalyst (i.e., a fixed bed reactor) would not teach or suggest to one skilled in the art to abandon that teaching in favor of conducting the oxidation reaction in a CSTR in which the N-(phosphonomethyl)iminodiacetic acid is continuously contacted with an oxygen source in the presence of a particulate catalyst that is subsequently filtered from the resulting product mixture as called for in claim 1. Moreover, one skilled in the art would expect the fixed bed reactor of Hershman et al. to operate at least partially in plug flow, thereby providing a favorable kinetic driving force for the oxidation both of N-(phosphonomethyl)iminodiacetic acid and C₁ by-products, formaldehyde and formic acid. The teachings of Hershman et al., therefore, would not render obvious the effectiveness of a CSTR system, each reactor of which operates under terminal conditions with respect to the conversion achieved therein.

In view of the above, applicants respectfully submit claim 100 and claims 101-199 depending directly or indirectly therefrom are patentable over the cited references.

Obviousness-Type Double Patenting Rejection

In response to the rejection of claims 57, 91, 144, 274 and 292 under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claim 1 of U.S.

- * Patent No. 6,603,039, applicants submit herewith a Terminal Disclaimer in compliance with 37 CFR 1.321(c). A check in
- * payment of the applicable fee under 37 CFR 1.20(d) is enclosed.

Conclusion

Favorable reconsideration and allowance of all pending claims are respectfully solicited.

Upon entry of this amendment, a total of 320 claims, including 15 independent claims, will be pending in the application. A check in payment of the applicable excess claims

* fee is enclosed.

The Commissioner is requested to charge any fee deficiency
in connection with this amendment to Deposit Account No. 19-1345.

Respectfully submitted,



Vincent M. Keil, Reg. No. 36,838
SENNIGER POWERS
One Metropolitan Square, 16th Floor
St. Louis, Missouri 63102
(314) 231-5400

VMK/ACW/lrw
*Enclosures

Express Mail Label No. EV 453250981 US
Mail Stop Amendment